

Magnetic properties of manganese-site substituted $Y(Cu,Mn)O_3$

O. PEÑA, D. GUTIÉRREZ*, P. DURÁN*, C. MOURE*

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511. CNRS - Univ. de Rennes 1 - Institut de Chimie de Rennes, 35042 Rennes cedex, FRANCE

*Instituto de Cerámica y Vidrio, CSIC, Departamento de Electrocerámica, Campus Universidad Autónoma de Madrid, 28049 Cantoblanco, Madrid, SPAIN

The magnetic properties of the solid solution $YCu_xMn_{1-x}O_3$ have been investigated in the whole range of possible substitutions $0.30 \leq x(Cu) \leq 0.50$. The $\chi_{a.c.}$ data showed the presence of minute amounts, undetectable by X-ray diffraction, of the antiferromagnetic $Y_2Cu_2O_5$ phase, which did not interfere with the overall magnetic behavior of the solid solution. The total effective moment of the paramagnetic state decreases continuously with $x(Cu)$. The average moment *per* Mn ion was estimated after subtraction of the copper contribution, giving approximately $4.4 \mu_B$, independent of the Cu concentration; this value corresponds to the magnetic moment expected for 50 % Mn^{3+} and 50 % Mn^{4+} . A paramagnetic-to-antiferromagnetic transition is observed at $T_{Neel} = 21$ K, also compositional-independent. The low temperature state, studied by ZFC/FC cycles and $M(H)$ loops, reinforce the idea of antiferromagnetic interactions in these compounds. A very small ferromagnetic component giving rise to low coercive fields of the order of 800 Oe, was present for all Cu concentrations. Additional nuclear powder diffraction measurements show no specific magnetic structure, suggesting short range interactions.

Keywords: perovskites, magnetic exchange, antiferromagnetism, substitution effects

Propiedades magnéticas de la manganita $Y(Cu,Mn)O_3$ sustituida en el sitio del manganeso

Se han investigado las propiedades magnéticas de la solución sólida $YCu_xMn_{1-x}O_3$ para todo el rango de posibles sustituciones $0.30 \leq x(Cu) \leq 0.50$. Las medidas de susceptibilidad $\chi_{a.c.}$ señalan la presencia de ínfimas cantidades de la fase antiferromagnética $Y_2Cu_2O_5$, la que no modifica las propiedades globales de la solución sólida. El momento magnético total del estado paramagnético decrece monótonamente con $x(Cu)$. El momento magnético promedio por ion Mn fue estimado después de sustraer la contribución del cobre, dando un valor aproximado de $4.4 \mu_B$, independiente de la concentración en cobre; este valor corresponde al momento magnético esperado para 50 % Mn^{3+} y 50 % Mn^{4+} . Una transición paramagnética hacia un estado antiferromagnético es observada a $T_{Neel} = 21$ K, independiente de la composición. Los estudios a bajas temperaturas, realizados mediante ciclos ZFC/FC y de magnetización $M(H)$, corroboran la idea de interacciones antiferromagnéticas en estos compuestos. Una pequeña componente ferromagnética es observada en los ciclos de magnetización realizados a 5K, indicando que el estado ordenado es principalmente de tipo antiferromagnético, con una componente inclinada despreciable, la que da lugar a un campo coercitivo muy pequeño (aprox. 800 Oe). Medidas preliminares por difracción de neutrones no indican ninguna estructura magnética específica, eliminando la posibilidad de interacciones de largo alcance.

Palabras clave: perovskitas, interacciones de canje, antiferromagnetismo, efectos de la sustitución

1. INTRODUCTION

Despite of the enormous amount of reports concerning the ferromagnetic manganites ABO_3 , of general formula $(RE,AE)MnO_3$ (AE = alkaline earth), very little is known about materials in which a partial substitution is made at the B (Mn) site. Nevertheless, a transformation mechanism $Mn^{3+} \rightarrow Mn^{4+}$ may also take place in these materials if the -initially- trivalent Mn atom is substituted by a divalent transition-metal element Me , leading to similar double-exchange interactions $Mn^{3+}-O-Mn^{4+}$. Indeed, for each divalent transition-metal ion incorporated into the structure, two manganese ions are involved at the same time: one which is being substituted, and another one, which will transform onto Mn^{4+} . From this basis, solid solutions of $RE(Me_xMn_{1-x})O_3$ type are limited to a maximum substitution rate of 50 % which leads, from electrical-charge equilibrium considerations, to a theoretical limit of $RE^{3+}Me_{0.5}^{2+}Mn_{0.5}^{4+}O_3$ [1].

Few reports have dealt with this type of substitution [2-4], but none was dealing with systematic studies within the whole domain of existence of the solid solution. Recently, we reported the crystallochemical, magnetic and transport properties aspects of the yttrium-based perovskites $Y(Me,Mn)O_3$, $Me = Co$ and Ni [5-8]. The copper case, $Me = Cu$, has been mainly considered from the chemical

and microstructural point of view, although some results have been also presented on electrical transport properties above room temperature [9]. In this work, we report the magnetic characterization of the copper-based solid solution $Y(Cu,Mn)O_3$, paying special attention to the magnetically ordered state.

2. EXPERIMENTAL

$YCu_xMn_{1-x}O_3$ compositions, of nominal concentrations $x(Cu)$ ranging from 0.0 up to 0.60, were prepared by solid state reaction of stoichiometric mixtures of reagent grade oxides. The mixtures were homogenized by wet attrition milling, calcined at 1000 °C for 1 hour. After additional grindings and mixing, powders were uniaxially pressed and sintered in air between 1100 °C and 1350 °C, for several cycles. X-ray diffraction (XRD) was performed using a Siemens 5000 diffractometer with CuK_α radiation. Lattice parameters were calculated from spectra obtained at a scanning rate of $1/2^\circ 2\theta/\text{min}$, using Si powder as an internal standard.

Magnetic measurements were performed using a SHE VTS-906 SQUID susceptometer, between 5 K and 300 K. All measurements

were done after cooling the samples in the absence of a magnetic field, applying then the desired field and warming the sample up to the maximum temperature (ZFC). This procedure was followed by cooling the sample under the same applied field (FC), thus performing a full zero-field cooled/field-cooled cycle ZFC/FC. Magnetization cycles $M(H)$ were performed at low temperatures, from -20 kOe up to +20 kOe. These properties were measured in specimens cut from ceramic bulks and glued to a thin rod in order to avoid disorientation due to torque forces exerted on the sample. Additional characterizations by a.c. techniques were performed using a home-made mutual-inductance susceptometer.

3. RESULTS AND DISCUSSION

3.1. Domain of homogeneity

XRD patterns were indexed according to a perovskite-type unit cell, with space group $Pbnm$. The perovskite phase formed in all cases, except for the non-substituted YMnO_3 manganite, which crystallizes in an hexagonal lattice (S.G. $P6_3cm$ [10]). At the nominal composition $x(\text{Cu}) = 0.2$, small quantities of YMnO_3 were found to coexist with the perovskite phase, thus delimiting a biphasic region comprised between $x = 0$ and $x \sim 0.20$. At the upper limit, for samples with $x(\text{Cu}) > 0.5$, impurity phases of Y_2O_3 and $\text{Y}_2\text{Cu}_2\text{O}_5$ were noticed, confirming the fact that the maximum substitution rate for a divalent ion like Cu^{2+} is limited to 50 at.% [1]. Table I summarizes the XRD results. More details about the crystallographic data can be found elsewhere [9].

TABLE I. LATTICE AND MAGNETIC PARAMETERS OF THE SOLID SOLUTION $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$

x	a $\pm 10^{-4}$ (nm)	b $\pm 10^{-4}$ (nm)	c $\pm 10^{-4}$ (nm)	V $\pm 4 \times 10^{-4}$ (nm ³)	Θ ± 2 [K]	$\mu_{\text{eff}} (\text{tot})$ ± 0.02 (μ_B)	μ_{eff} Mn-lattice (μ_B) ^b	μ Mn-atom (μ_B) ^c
0.20 ^a	0.5246	0.5730	0.7382	0.2219	- a -	- a -	- a -	- a -
0.30	0.5253	0.5719	0.7363	0.2212	10	3.81	3.69	4.41
0.33	0.5256	0.5715	0.7362	0.2211	10	3.74	3.60	4.40
0.40	0.5247	0.5718	0.7367	0.2211	11	3.60	3.43	4.43
0.45	0.5247	0.5714	0.7371	0.2210	12	3.47	3.27	4.41
0.50	0.5246	0.5722	0.7368	0.2212	15	3.37	3.14	4.44

(a) biphasic region

(b) magnetic contribution of the Mn-sublattice, deduced from $\mu_{\text{Mn}} = [\mu_{\text{eff}}^2 - \mu_{\text{Cu}}^2]^{1/2} = [\mu_{\text{eff}}^2 - 1.73^2]^{1/2}$

(c) magnetic moment per Mn-atom (normalized to the $(1-x)$ Mn content)

According to Table I, the lattice parameters stay relative constant and rather independent of the copper concentration, in contrast to the observations in the analogous systems with $\text{Me} = \text{Co}$ and Ni [6-7]. Indeed, contrary to Ni^{2+} and Co^{2+} , Cu^{2+} is a Jahn-Teller (JT) ion, such as the JT Mn^{3+} cation. Since the main cause of the lattice's modifications comes from the disappearance of the JT-type ions, the number of such ions which disappear during the partial substitution of Mn^{3+} by Cu^{2+} is lower than in the cases of Ni or Co substitutions, resulting in a less pronounced variation of the lattice parameters [1]. From the crystallographic data we may propose the existence of a pure perovskite-phase within the range $[0.30 \leq x \leq 0.50]$; consequently, our magnetic measurements were limited to this region. However, as we will see latter, minute amounts of the very stable compound $\text{Y}_2\text{Cu}_2\text{O}_5$, usually present in oxide materials like bismuth or yttrium cuprates [11-13], may still be present in this series. Such impurities were completely undetectable by XRD techniques, meaning that its content should be less than 3-4 wt.% of the overall sample.

3.2. Magnetic measurements

3.2.1. PARAMAGNETIC REGIME

Figure 1 shows the inverse magnetic susceptibility measured at 1 kOe, between 5 K and 300 K, for the perovskite-phase samples $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$, $0.30 \leq x \leq 0.50$. A perfectly linear variation of χ^{-1} with T is observed between $T \sim 40$ K and room temperature. Deviations to the Curie-Weiss behavior are observed at lower temperatures at the approach of the magnetically ordered regime.

The magnetic parameters (μ_{eff} and Θ) derived from a Curie-Weiss fit are listed in Table I. The effective moment μ_{eff} decreases linearly with increasing content of copper, in contrast to the non-monotonic variations observed in the Co- and Ni-based $\text{Y}(\text{Me},\text{Mn})\text{O}_3$ perovskites [5,8]. Assuming a high stability of the d^9 configuration of the copper $2+$ ion, we may readily calculate the Mn contribution to the total moment, by using the following relation:

$$\mu_{\text{Mn}} = [\mu_{\text{eff}}^2 - \mu_{\text{Cu}}^2]^{1/2} = [\mu_{\text{eff}}^2 - 1.73^2]^{1/2}.$$

Results are given in Table I, together with the magnetic moment per Mn ion ($\mu/\text{Mn-atom}$), this latter obtained by normalizing the Mn-lattice contribution by the actual manganese content $(1-x)$. Quite surprisingly, the average moment of Mn stays constant over the whole series, with a mean value of $4.42 \pm 0.02 \mu_B$, which corresponds exactly to the expected value for equal amounts, 50 % each, of Mn^{3+} and Mn^{4+} ($\mu_{\text{ave}} = 4.42 \mu_B$). However, such a situation is found only at the optimum substituent concentration, that is for $x = 1/3$, for which the charge-equilibrium relation must be $\text{Y}^{3+}[\text{Cu}_{1/3}^{2+}(\text{Mn}_{0.5}^{3+}\text{Mn}_{0.5}^{4+})]\text{O}_3^{2-}$. The expected values of μ_{ave} of manganese, for the other compositions, should go from $4.5 \mu_B$ (at $x = 0.3$) down to $3.9 \mu_B$ (at $x = 0.5$), not far from the experimental value of $4.42 \mu_B$, but still outside the error bar. One possible explanation may come from oxygen deficiencies which may create additional Mn^{3+} ions in the Mn sublattice, yielding larger moments than expected. However, the thermal cycling followed during synthesis and annealing was rigorously controlled and therefore the oxygen concentration for all samples should be identical. Thus, we have no readily explanation available at this moment to explain such constant effective moment throughout the solid solution.

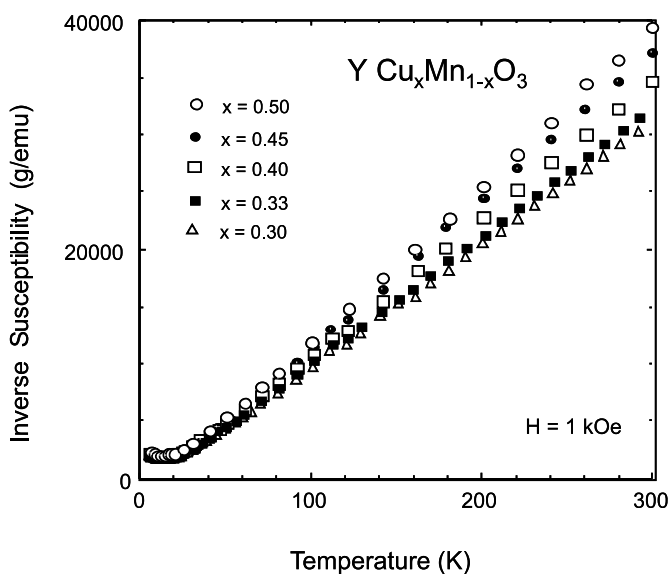


Fig. 1. Inverse susceptibility of $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$ samples, measured at 1 kOe

3.2.2. ORDERED REGIME

Figure 2 shows the a.c. susceptibility measured in the range $[4 \text{ K} \leq T \leq 30 \text{ K}]$, under an applied a.c. field of about 30-50 mOe. Curves have been Y-shifted for clarity. Two magnetic transitions are observed, centered at about 11-12 K ($T_{\max}^{(1)}$) and 20-21 K ($T_{\max}^{(2)}$), for all samples. The same two transitions are also observed by d.c. susceptibility, under low applied fields. It is clearly seen from fig. 2, that the amplitude of the lowest transition increases with the $x(\text{Cu})$ concentration, staying always at the same temperature value. Since $T_{\max}^{(1)}$ strongly resembles the antiferromagnetic ordering temperature of the impurity phase $\text{Y}_2\text{Cu}_2\text{O}_5$ occurring at 13 K [14,15], additional samples were prepared by mechanical mixing of very pure YMnO_3 and $\text{Y}_2\text{Cu}_2\text{O}_5$ phases and measured under the same experimental conditions as the $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$ series. Some results are shown in figure 3, for samples with a molar ratio of 0, 2, 5 and 15 % of $\text{Y}_2\text{Cu}_2\text{O}_5$ in the sample. It is indeed quite clear that the anomaly observed at $T_{\max}^{(1)}$ is certainly due to minute amounts of such impurity phase, which can not be detected by XRD. Neutron diffraction data obtained in a sample of nominal concentration $\text{YCu}_{0.40}\text{Mn}_{0.60}\text{O}_3$ shows, furthermore, the presence of only one magnetic peak below 12 K, superposed to the nuclear spectra of the perovskite phase [16].

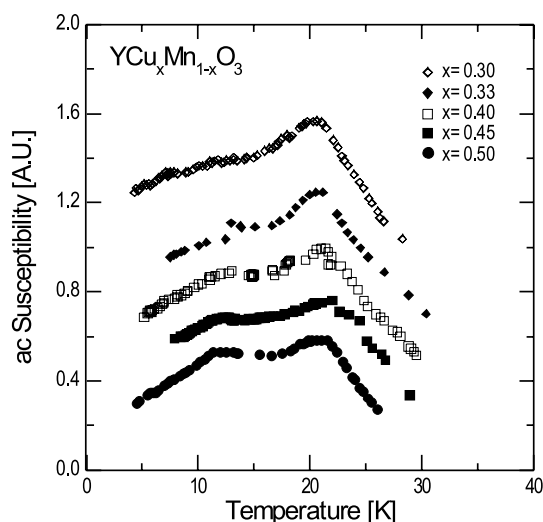


Fig. 2. a.c. susceptibility of $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$ samples (shift of Y-axis, for clarity)

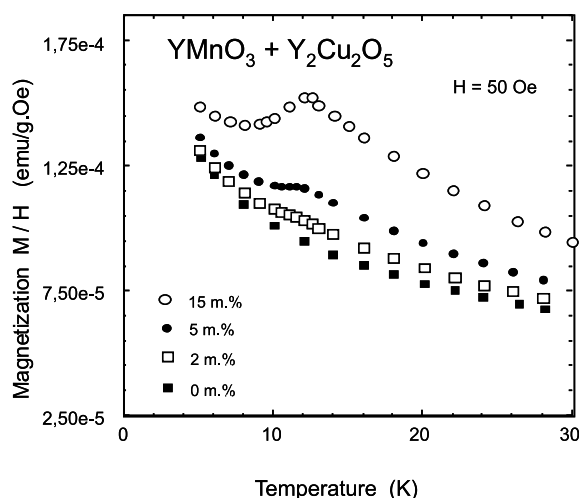


Fig. 3. Temperature dependence of the M/H ratio measured at 50 Oe, for 4 samples prepared by mechanical mixing of YMnO_3 and $\text{Y}_2\text{Cu}_2\text{O}_5$: 0, 2, 5 and 15 m.% mean the molar concentration of the $\text{Y}_2\text{Cu}_2\text{O}_5$ phase

Confident that the transition at $T_{\max}^{(1)}$ is due to an impurity phase, we performed ZFC/FC cycles at different applied magnetic fields. Figure 4 shows the magnetic behavior of three samples, with nominal $x(\text{Cu}) = 0.3, 0.33$ and 0.45 . A net irreversibility, likely of antiferromagnetic or spin-glass nature, appears immediately below $T_{\max}^{(2)}$ and extends down to $T_{\max}^{(1)}$. Indeed, if a rough subtraction is made of the impurities contribution, the resulting magnetization stays constant or increases slightly with decreasing temperature, precluding the existence of strong ferromagnetic interactions. This is further confirmed by magnetization loops $M(H)$ performed at 5 K (fig. 5), which show predominant antiferromagnetic interactions (almost linear field dependence M -versus- H) and a very weak ferromagnetic component. Nuclear diffraction experiments performed between 30 K and 1.4 K did not show any magnetic structure, either due to a bad crystallization of the specimen or to short-range interactions (like spin-glass effects) [16]. A similar situation has been reported in $(\text{La,Sr})\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ in which, at high doping of Cu, an electronic phase separation and a spin-glass phase were proposed, with no long-range ferromagnetic interactions [17]. Current work is aimed towards a better understanding of the magnetic behavior at low temperatures.

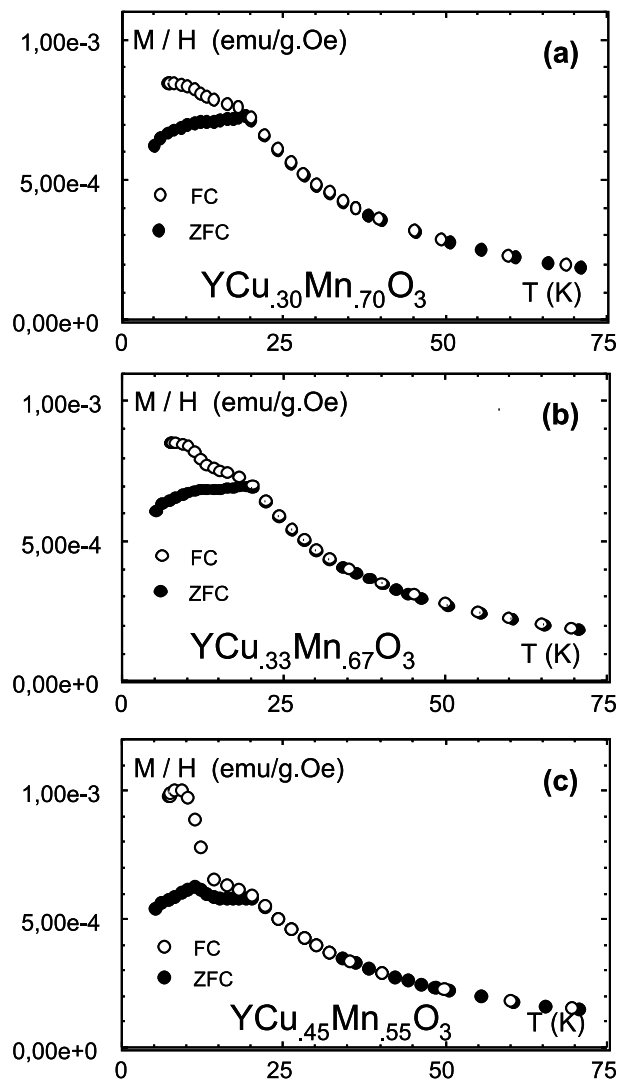


Fig. 4. Thermal variation of the M/H ratio for three samples of $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$ during a ZFC/FC cycle performed under a 50-Oe applied field: (a) $x = 0.3$, (b) $x = 0.33$, (c) $x = 0.45$.

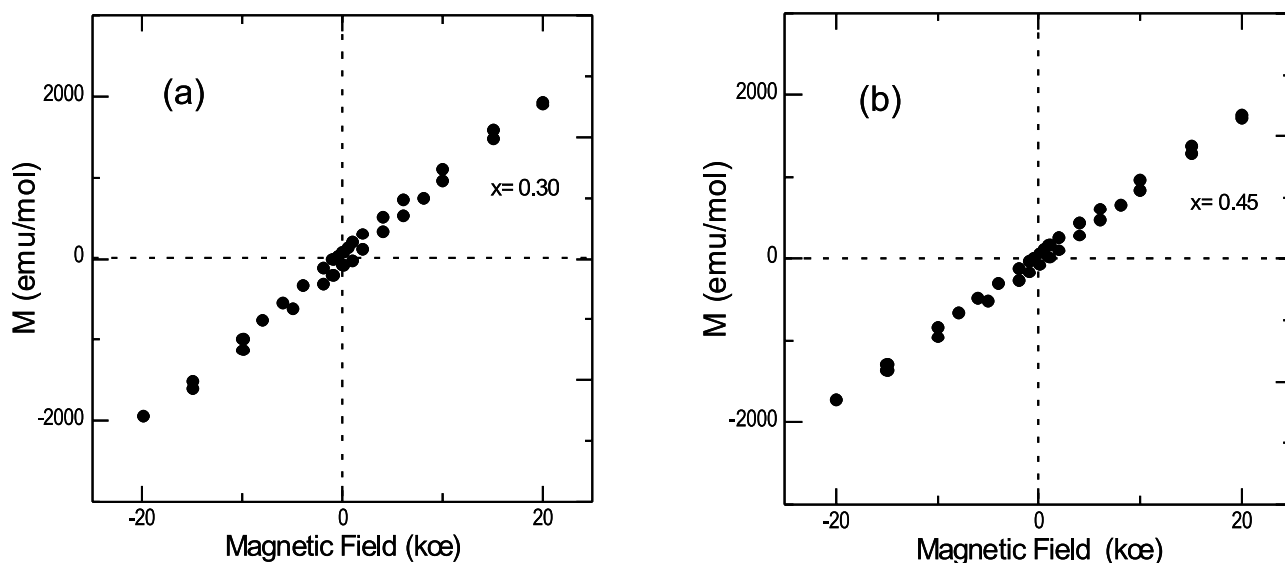


Fig. 5 . Magnetization cycles $M(H)$ measured at $T = 5$ K, for two samples of $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$: (a) $x = 0.30$, (b) $x = 0.45$

4. CONCLUSIONS

The substitution of Mn^{3+} by Cu^{2+} in the hexagonal YMnO_3 compound leads to a phase transition from the hexagonal phase to an orthorhombic (O'-type) perovskite phase at about $x(\text{Cu}) \sim 0.20$. The domain of homogeneity of the perovskite appears to be $[0.3 \leq x \leq 0.5]$, although minute amounts of a stable yttrium-copper-oxide were still present. These impurities, undetectable by classical diffraction techniques, were evidenced by low temperature nuclear powder diffraction measurements (magnetic peak below 12 K) and by inductive techniques (double magnetic transition at low temperatures). We propose that such impurities correspond to the antiferromagnetic $\text{Y}_2\text{Cu}_2\text{O}_5$ compound.

After subtraction of the impurity contribution, the magnetic properties of the normal and ordered states of the $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$ perovskite compounds have been thoroughly determined. It is found that the average magnetic moment of the Mn ion is approximately $4.4 \mu_B$, which corresponds to the value expected for 50 % Mn^{3+} and 50 % Mn^{4+} . The low temperature state is characterized by an antiferromagnetic (or spin-glass) order occurring at 20-21 K, independent of the copper concentration. ZFC/FC cycles and magnetization loops reinforce the idea of antiferromagnetic interactions in these compounds, with a very small ferromagnetic component giving rise to low coercive fields, of the order of 800 Oe. Additional nuclear powder diffraction measurements show no specific magnetic structure, suggesting short range interactions.

REFERENCES

1. C. Moure, D. Gutierrez, O. Peña, P. Duran. "Structural characterization of $\text{YMe}_x\text{Mn}_{1-x}\text{O}_3$ ($\text{Me} = \text{Cu, Ni, Co}$) perovskites". *J. Solid State Chem.*, **163**, 377-384 (2002)
2. N. Gayathri, A.K. Raychaudhuri, S.K. Tiwary, R. Gundakaram, A. Arulraj, C.N.R. Rao. "Electrical transport, magnetism, and magnetoresistance in ferromagnetic oxides with mixed exchange interactions : a study of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ system". *Phys. Rev. B*, **56**, 1345-1353 (1997)
3. Z. Yang, L. Ye, X. Xie. "Electronic and magnetic properties of the perovskite oxides: $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ ". *Phys. Rev. B*, **59**, 7051-7057 (1999)
4. K. Ghosh, S.B. Ogale, R. Ramesh, R.L. Greene, T. Venkatesan, K.M. Gapchup, R. Bathe, S.I. Patil. "Transition-element doping effects in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ". *Phys. Rev. B*, **59**, 533-537 (1999)
5. O. Peña, M. Bahout, D. Gutierrez, J.F. Fernandez, P. Duran, C. Moure. "Critical behavior in the perovskite-like system $\text{Y}(\text{Ni,Mn})\text{O}_3$ ". *J. Phys. Chem. Solids*, **61**, 2019-2024 (2000)
6. D. Gutierrez, O. Peña, P. Duran, C. Moure. "Crystal structure, electrical conductivity and Seebeck coefficient of $\text{Y}(\text{Ni,Mn})\text{O}_3$ solid solution". *J. Eur. Ceram. Soc.*, **22**, 567-572 (2002)
7. D. Gutierrez, O. Peña, P. Duran, C. Moure. "Crystalline structure and electrical properties of $\text{YCo}_x\text{Mn}_{1-x}\text{O}_3$ solid solutions". *J. Eur. Ceram. Soc.*, **22**, 1257-1262 (2002)
8. D. Gutierrez, O. Peña, K. Ghanimi, P. Duran, C. Moure. "Electrical and magnetic features in the perovskite-type system $\text{Y}(\text{Co,Mn})\text{O}_3$ ". *J. Phys. Chem. Solids*, **63**, 1975-1982 (2002)
9. D. Gutierrez, O. Peña, P. Duran, C. Moure. "Crystalline structure and electrical properties of $\text{YCu}_x\text{Mn}_{1-x}\text{O}_3$ solid solutions". *J. Eur. Ceram. Soc.*, **22**, 2939-2944 (2002)
10. H.L. Yakel, W.C. Koehler, E.F. Bertaut, E.F. Forrat. "On the crystal structure of the manganese(III) trioxides of the heavy lanthanides and yttrium". *Acta Crystallogr.*, **16**, 957-962 (1963)
11. Y. Ando, K. Fukuda, S. Kondoh, M. Sera, M. Onoda, M. Sato. "Study of normal and superconducting properties of $\text{Bi}_2\text{Sr}_3(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_4\text{O}_y$ ". *Solid State Commun.*, **67**, 815-819 (1988)
12. R. Yoshizaki, Y. Saito, Y. Abe, H. Ikeda. "Superconducting and magnetic properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($0 \leq x \leq 1$)". *Physica C*, **152**, 408-412 (1988)
13. T. Tamegai, K. Koga, K. Suzuki, M. Ichihara, F. Sakai, Y. Iye. "Metal-insulator transition in the $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$ system". *Jap. J. Appl. Phys.*, **28**, L112-L115, (1989)
14. R. Troc, Z. Bukowski, R. Horyn, J. Klamut. "Possible antiferromagnetic ordering in $\text{Y}_2\text{Cu}_2\text{O}_5$. Paramagnetic behaviour of BaCuO_2 ". *Phys. Lett. A*, **125**, 222-224 (1987)
15. E. Laxmi Narsaiah, U.V. Subba Rao, O. Peña, M. Sergent. "Substitution effects of yttrium in the BISCCO (2212) system". *Mat. Chem. Phys.*, **33**, 58-62 (1993)
16. O. Peña, M. Bahout, G. André, C. Moure, D. Gutierrez, unpublished
17. Lei Zheng, Xiaojun Xu, Li Pi, Yuheng Zhang. "Observation of electronic phase separation in $\text{La}_{0.825}\text{Sr}_{0.175}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ perovskites". *Phys. Rev. B*, **62**, 1193-1196 (2000)